

UNIVERSITI TEKNOLOGI MARA

**PREPARATION AND
CHARACTERIZATION OF
EPOXIDIZED-30% POLY (METHYL
METHACRYLATE)-GRAFTED
NATURAL RUBBER POLYMER
ELECTROLYTES FOR
ELECTROCHEMICAL DOUBLE
LAYER SUPERCAPACITOR**

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of the requirements for the degree of
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AUTHOR'S DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Teknologi MARA. It is original and is the result of my own work, unless otherwise indicated or acknowledged as referenced work. This thesis has not been submitted to any other academic institution or non-academic institution for any other degree or qualification.

I, hereby, acknowledge that I have been supplied with the Academic Rules and Regulations for Post Graduate, Universiti Teknologi MARA, regulating the conduct of my study and research.

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ABSTRACT

This dissertation focuses on the preparation and characterization of epoxidized- 30% poly(methyl methacrylate) grafted natural rubber (EMG30)-salt complexes and plasticized EMG30-salt complexes. In the present study, EMG30 as polymer host, lithium trifluoromethanesulfonate (LiCF_3SO_3) as doping salt and ethylene carbonate (EC) as a plasticizer were used in the preparation of solid polymer electrolytes (SPEs) and gel polymer electrolytes (GPEs). The EMG30 was prepared by performic epoxidation method with various time reaction. Proton nuclear magnetic resonance ($^1\text{H NMR}$) and Fourier transform infrared spectroscopy (FTIR) spectra confirm a new peak at 2.70-2.71 ppm and 871 cm^{-1} which were assigned to the epoxy group. 54.6, 62.3 and 50.0 mol% of epoxidation content were obtained in EMG30 at 6, 9 and 12 hours of time reactions, respectively. SPEs and GPEs based on EMG30 were prepared by the solution cast technique with different weight percent (wt.%) of LiCF_3SO_3 and EC. FTIR spectroscopy studies have shown that coordination of Li^+ ions has occurred on the oxygen (O) atom in the carbonyl (C=O) group, ether group (O-CH_3) and epoxy (C-O-C) group of EMG30. X-ray diffraction (XRD) analysis confirmed amorphous nature of EMG30 samples. Thermogravimetric analysis (TGA) have shown that thermal stability of EMG30 is increased compared to pure MG30. The differential scanning calorimetry (DSC) analysis found the epoxidation reaction has increased the T_g value of EMG30 ($T_g \approx -39.1\text{ }^\circ\text{C}$) due to the restriction of hydrogen bonding. The morphology of the samples has also been investigated using Field-emission scanning electron microscopy (FESEM). EMG30 structure shows the homogeneity and there is no trace of phase separation could be observed by either physical observation or FESEM micrograph. The conductivity of the samples was characterized by the impedance spectroscopy in the frequency range between 100 Hz and 1 MHz. The highest ionic conductivity of SPE containing 40 wt.% LiCF_3SO_3 in 62.3 mol% EMG30 was $1.10 \times 10^{-3}\text{ S.cm}^{-1}$, which is two orders of magnitude higher than MG30- LiCF_3SO_3 complexes. Further enhancement of ionic conductivity 62.3 mol% EMG30- LiCF_3SO_3 obtained with addition of plasticizer into SPE was $4.83 \times 10^{-3}\text{ S.cm}^{-1}$ at 50 wt.% EC in 62.3 mol% EMG30- LiCF_3SO_3 . Ionic conductivity for all systems was also studied as a function of temperature from 303 K up to 373 K. The plot of $\log \sigma$ versus $1000/(T-T_0)$ for each sample obey VTF behavior. The ionic transference number of the SPE and GPE system studied was found to be ~ 0.83 and ~ 0.96 , respectively. These results reveal that both systems were predominantly due to ions and only negligible contribution came from electron. The window stability of 62.3 mol% EMG30 based on SPE was observed around 1.8 V versus SS and 3.02 versus Li^+/Li whereas the window stability of GPE was around 2.9 V versus SS and 4.5 V versus Li^+/Li . The highest conducting of SPE and GPE were chosen as an electrolyte in electrochemical double layer capacitor (EDLC). EDLC containing GPE exhibits the most stable performance with higher specific capacitance value (0.470 F g^{-1}) and can maintain its electrochemical stability over 100 cycles of charge and discharge processes. The highest power density (P) and energy density (E) were found to be 7.49 W kg^{-1} and 9.71 Wh kg^{-1} .

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